

Microscale Distribution and Speciation of Trace Elements in Soil

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INTRODUCTION

The availability of nutrients and toxic elements are key factors that control soil quality and affect soil management strategies. To determine the availability of chemical elements in soils, it is critical that the chemical speciation and reaction mechanisms of elements be understood. In this study we examine the distribution of trace elements and mineral associations in soil samples using synchrotron based X-ray fluorescence microprobe and determine the oxidation state and local atomic structure using X-ray absorption spectroscopy. In particular, this study focuses on the trace elements arsenic and selenium, and their associations with the iron minerals jarosite and goethite. The findings of this research will provide a better understanding of trace element cycling in a natural, unaltered, soil environment.

METHODS

To preserve the morphology and aggregate distribution the soils were collected using a soil-coring device. They were air dried at 35°C and then impregnated with LR White resin under a vacuum. The samples were then cured in an oven at 60°C for 24-48 hrs to induce resin hardening. The samples were then cut into 2x3x0.25 cm pieces using a diamond edged saw, after which they were ground to various thickness (0.5-3 mm). This preparation procedure results in small wafers with morphologies intact that are sufficiently thin enough to minimize self-absorption and flat enough so that the plane of focus is constant. The samples were analyzed on beamlines 10.3.1 and 10.3.2 at the Advanced Light Source. The data from the x-ray microprobe were collected in 10 micron steps, corrected for background, and normalized to a NIST standard with known elemental concentrations. The units of the data are $\mu\text{g}/\text{cm}^2$, and allow for relative comparisons only. The data were mapped using the contour mapping options available in the program Microcal OriginTM. For the micro-XAFS data the scans were collected using 0.4 eV steps at 0.5 to 15 seconds per step. The XAFS scans presented are the average of 10 to 20 scans.

RESULTS

The spatial distributions of Fe, As, Se, S, P and K of a soil sample are shown in Fig. 1. The iron mineral distribution can be inferred by evaluating the distributions of Fe, S, and K. There are two distinct mineral aggregates located in this soil section. The mineral aggregates labeled A are most likely an iron oxide such as goethite or ferrihydrite. These features have a red/orange color that is characteristic of iron oxide minerals. The mineral aggregate labeled B is high in Fe, K, and S, indicating that it has the elemental composition indicative of the iron sulfate mineral jarosite. Mineral aggregate B has a yellow brown color that is characteristic of the jarosite mineral. Thus, by using the microprobe we have identified two distinct iron minerals that are only a few microns apart from each other. Similar features have been identified in other soil thin sections collected nearby (within 20 meters). These mineral aggregates tend to have diameters of 10-500 microns, and comprise approximately 20% of the soil matrix. To gain additional information on the mineral identity we have collected the Fe EXAFS spectra from the iron oxide and iron sulfur features. The chi structures for the two mineral aggregates are presented in Fig. 2. There are distinct differences in the two spectra that indicate that the atomic structure of the two mineral aggregates is unique. These EXAFS data will be compared to reference minerals (pure minerals) to gain additional confirmation on the mineral identities of the two aggregates.

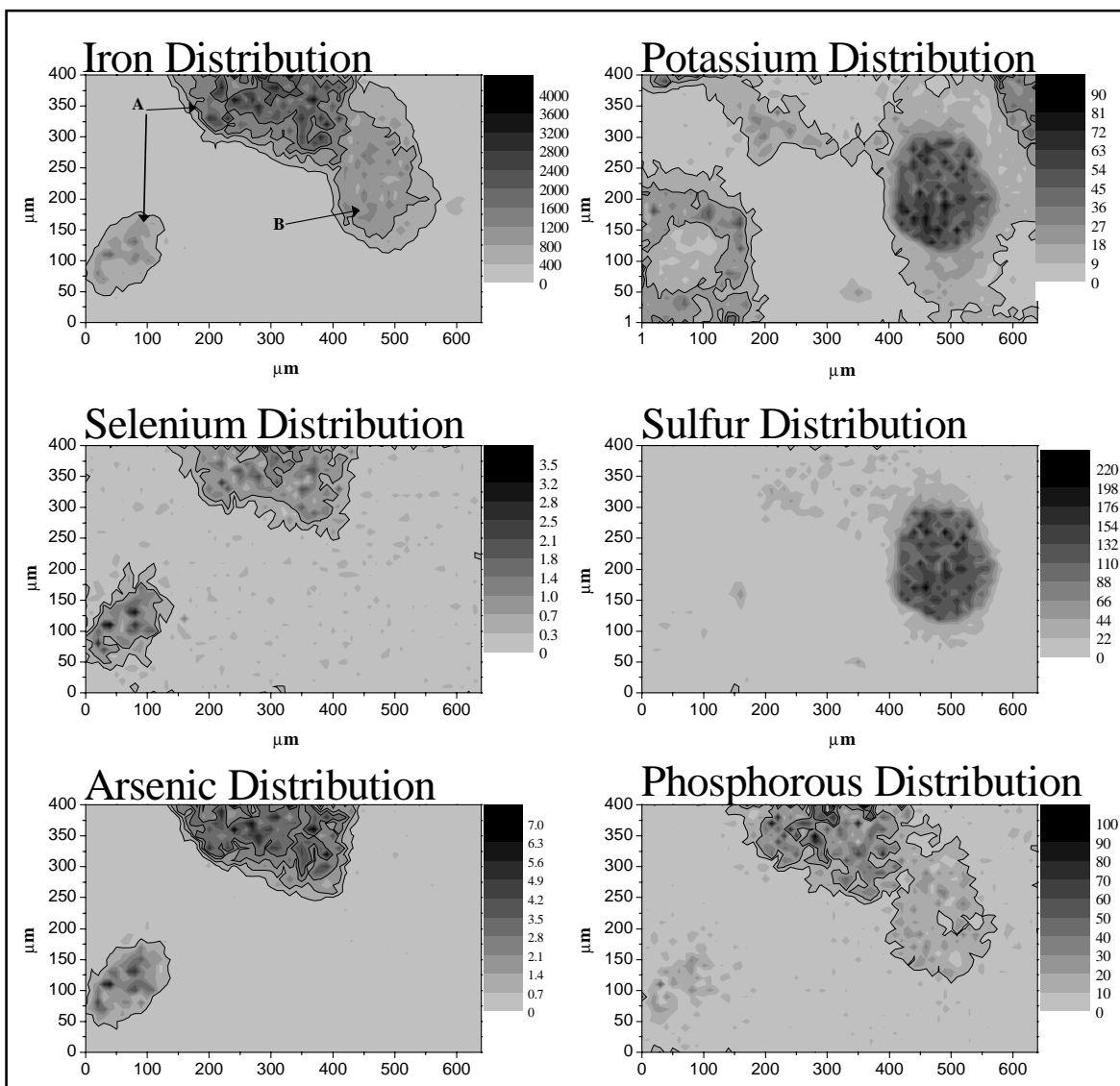


Fig. 1 Spatial distribution of selected elements in soil thin section. Feature A, goethite or ferrihydrite and Feature B, jarosite.

Comparison of the spatial distribution of the trace elements As and Se (Fig. 1) with the two iron mineral aggregates indicate that these trace elements are preferentially associated with the iron oxide minerals, and have very little partitioning in the iron sulfur and the matrix features. In contrast to the Se and As, the distribution of P in the soil shows no preference between the iron oxide or iron sulfur mineral aggregates. To determine the oxidation state of the As in the iron oxide aggregates the XANES spectrum was collected (Fig. 3). Comparison of the edge position of this spectrum with As(III) and As(V) reference spectra indicate that the oxidation state of the As in the iron oxide aggregate is five. Obtaining similar information about oxidation state of the Se in the soil is an area that is currently being researched.

The research conducted on beamlines 10.3.1 and 10.3.2 has provided unique information on the speciation of As and Se in soils. In particular, the use of the high intensity photons generated by the ALS has enabled the elemental mapping of the trace elements that comprise less than 0.002 % (mass basis) of the soil material. In addition, these results show the ability of the microprobe on beamline 10.3.2 to collect distinct XAFS spectra in heterogeneous samples in which the mineral aggregates are separated by only a few microns. This is not possible without the

microprobe capabilities of the beamline. The research done on these beamlines has provided important information on trace element cycling in the environment.

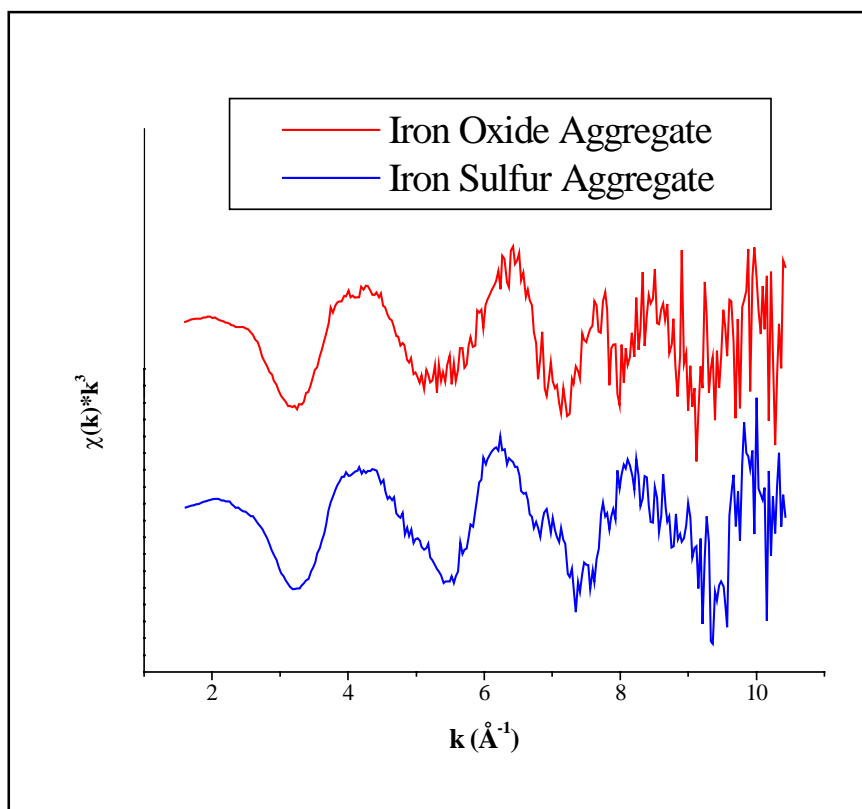


Fig. 2 EXAFS chi structure from aggregates A (iron oxide) and B (iron sulfur) in soil.

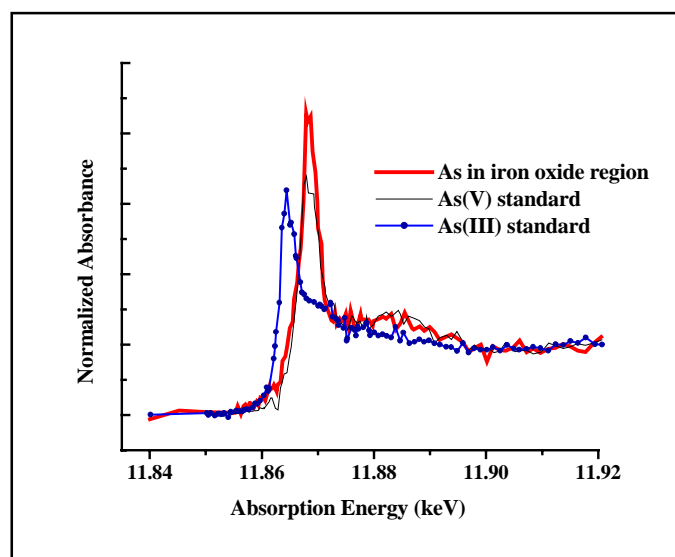


Fig. 3 Arsenic XANES spectra from aggregate A (iron oxide).

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